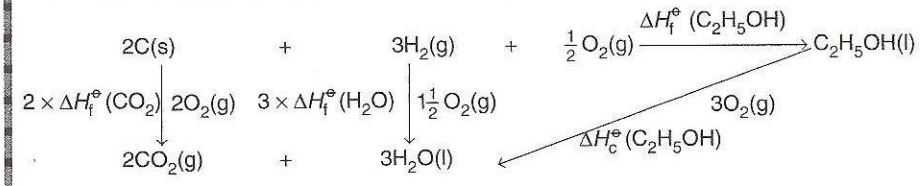
HL Energy cycles

STANDARD ENTHALPY CHANGE OF FORMATION $\Delta H_f^\ominus$

The standard enthalpy change of formation of a compound is the enthalpy change when one mole of the compound is formed from its elements in their standard states at 298 K and 1 atm pressure.

From this it follows that $\Delta H_f^\ominus$ for an element in its standard state will be zero.

An accurate value for the standard enthalpy change of formation of ethanol can be determined from the following cycle.

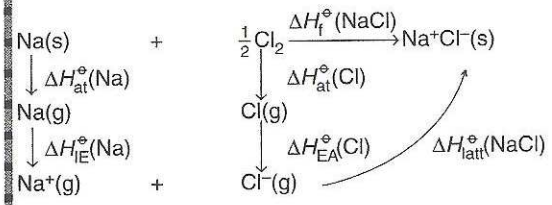


By Hess' law: $\Delta H_f^\ominus(C_2H_5OH) = 2 \times \Delta H_f^\ominus(CO_2) + 3 \times \Delta H_f^\ominus(H_2O) - \Delta H_c^\ominus(C_2H_5OH)$

Substituting the relevant values $\Delta H_f^\ominus(C_2H_5OH) = (2 \times -393.5) + (3 \times -285.8) - (-1371) = -273.4$ kJ mol^{-1}

BORN–HABER CYCLES

Born–Haber cycles are simply energy cycles for the formation of ionic compounds. The enthalpy change of formation of sodium chloride can be considered to occur through a number of separate steps.



Using Hess' law:

$\Delta H_f^\ominus(NaCl) = \Delta H_{at}^\ominus(Na) + \Delta H_{IE}^\ominus(Na) + \Delta H_{at}^\ominus(Cl) + \Delta H_{EA}^\ominus(Cl) + \Delta H_{latt}^\ominus(NaCl)$

Substituting the relevant values:

$\Delta H_f^\ominus(NaCl) = +108 + 494 + 121 - 364 - 771 = -412$ kJ mol^{-1}

Note: it is the large lattice enthalpy that mainly compensates for the endothermic processes and leads to the enthalpy of formation of ionic compounds having a negative value.

LATTICE ENTHALPY $\Delta H_{latt}^\ominus$

The lattice enthalpy relates either to the endothermic process of turning a crystalline solid into its gaseous ions or to the exothermic process of turning gaseous ions into a crystalline solid.

$MX(s) \rightleftharpoons M^+(g) + X^-(g)$

The sign of the lattice enthalpy indicates whether the lattice is being formed (–) or broken (+).

The size of the lattice enthalpy depends both on the size of the ions and on the charge carried by the ions.

cation size increasing →			anion size increasing →		
LiCl	NaCl	KCl	NaCl	NaBr	NaI
Lattice enthalpy / kJ mol^{-1}					
846	771	701	771	733	684

charge on cation increasing →		charge on anion increasing →	
NaCl	$MgCl_2$	$MgCl_2$	MgO
Lattice enthalpy / kJ mol^{-1}			
771	2493	2493	3889

ENTHALPY OF ATOMIZATION $\Delta H_{at}^\ominus$

The standard enthalpy of atomization is the standard enthalpy change when one mole of gaseous atoms is formed from the element in its standard state under standard conditions. For diatomic molecules this is equal to half the bond dissociation enthalpy.

$\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$ $\quad \Delta H_{at}^\ominus = +121$ kJ mol^{-1}

ELECTRON AFFINITY $\Delta H_{EA}^\ominus$

The electron affinity is the enthalpy change when an electron is added to an isolated atom in the gaseous state, i.e.

$X(g) + e \rightarrow X^-(g)$

Atoms 'want' an extra electron so electron affinity values are negative for the first electron. However, when oxygen forms the O^{2-} ion the overall process is endothermic:

$O(g) + e \rightarrow O^-(g)$	$\Delta H^\ominus = -142$ kJ mol^{-1}
$O^-(g) + e \rightarrow O^{2-}(g)$	$\Delta H^\ominus = +844$ kJ mol^{-1}
overall $O(g) + 2e \rightarrow O^{2-}(g)$	$\Delta H^\ominus = +702$ kJ mol^{-1}

USE OF BORN–HABER CYCLES

Like any energy cycle Born–Haber cycles can be used to find the value of an unknown. They can also be used to assess how ionic a substance is. The lattice enthalpy can be calculated theoretically by considering the charge and size of the constituent ions. It can also be obtained indirectly from the Born–Haber cycle. If there is good agreement between the two values then it is reasonable to assume that there is a high degree of ionic character, e.g. NaCl. However, if there is a big difference between the two values then it is because the compounds possesses a considerable degree of covalent character, e.g. AgCl.

	NaCl	AgCl
Theoretical value / kJ mol^{-1}	766	770
Experimental value / kJ mol^{-1}	771	905